Room temperature "super-cooling" of water by interaction with hydrophobic groups in a lipidic gel

F. Betancourt[1], F. Burkard[1], and R. Glaeser[1,2,3]

[1]Life Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

[2]Department of Molecular and Cell Biology, University of California, Berkeley, California 94720, USA

INTRODUCTION

In a preliminary study of the behavior of liquid and frozen water we collected FTIR spectra from thin layers of i) water alone or ii) water incorporated into a lipidic cubic phase gel formed with monoolein, a monoacyl glyceride. The position of the OH-stretch peak reflects hydrogen bonding strength between water molecules. Spectra taken at room temperature reveal that water trapped in the lipid matrix of the gel behaves as though it were supercooled, providing the water:lipid ratio is low. Water incorporated into lipidic gels may serve as a simple but instructive model for water trapped in the hydrophobic crevices or channels of proteins such as enzymes and ion pumps.

RESULTS

The use of a sealed, vacuum-tight sample holder designed to fit a Thompson-Joule refrigerator allowed us to collect Fourier Transform IR (FTIR) spectra from thin films of either water or gels formed from water and mono-olein at temperatures ranging from 298K to 200K. The disruption of hydrogen bonds in liquid water by a dissolved salt (KBr) is apparent in Figure 1. The OH stretch peak at about 3400 cm^{-1} is shifted to a higher wavenumber in a solution of KBR compared to pure water, reflecting greater occupancy of higher energy vibrational states.

In pure water, hydrogen bonding acts to dampen the OH stretch vibrational mode. As water is cooled this dampening effect appears to increase, reflected in the shift of the OH stretch peak to lower wavenumbers (Figure 2, Table I). Below 250K we observed that this shift was particularly dramatic , and was accompanied by an abrupt change in the shape of the peak. We believe that this indicates a phase transitioin from the liquid to the frozen state between 250K and 240K. (Tiny droplets of water have been shown to spontaneously freeze at about 235K [Koop et al., Nature 406, 611].) From this it follows that our water samples are supercooled between 270K and 250K.

FTIR spectroscopy of gels formed by mixtures of water and mono-olein reveals a similar dampening effect as the ratio of water to lipid decreases (Figure 3, Table II). Gels formed by water and mono-olein have a structure in which water is trapped in what are in effect lipid bilayer tunnels. These data suggest that at low ratios of water to lipid, water molecules in these tunnels become relatively immobilized, as in the supercooled state, and thus experience stonger hydrogen bonding. A plausible explanation is that at these low ratios, a high proportion of water molecules are recruited to participate in some sort of structure around hydrophobic groups of the lipid. The OH stretch peak value of about 3260 suggests that this structure bears some similarity to that of supercooled water (compare Tables I and II). We note also that at the lowest ratio tested, a gel could not be formed. Since water was not trapped in hydrophobic tunnels in this case, the 0H stretch peak is "normal" for bulk liquid water, i.e., near 3400 cm-1. Similarly, at the highest ratio, the preponderance of water molecules are truly in a bulk liquid phase.

FIGURE CAPTIONS

Figure 1. FTIR spctra of pure water (solid line) and an aqueous solution of KBr (dotted line). The latter was obtained from a commercial library of IR spectra.
Figure 2. FTIR spctra of water cooled from 298K to 200K.
Table I. Summarization of the data presented in Figure 2.
Figure 3. FTIR spctra of mixtures of water and mono-olein. After prolonged centrifugation, these mixtures form homogeneous gels or liquids.
Table I. Summarization of the data presented in Figure 3.

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Principal investigator: Felicia Betancourt, Advanced Light Source, Lawrence Berkeley National Laboratory. Email: fmh@xtalu.lbl.gov. Telephone: 510-486-6597.

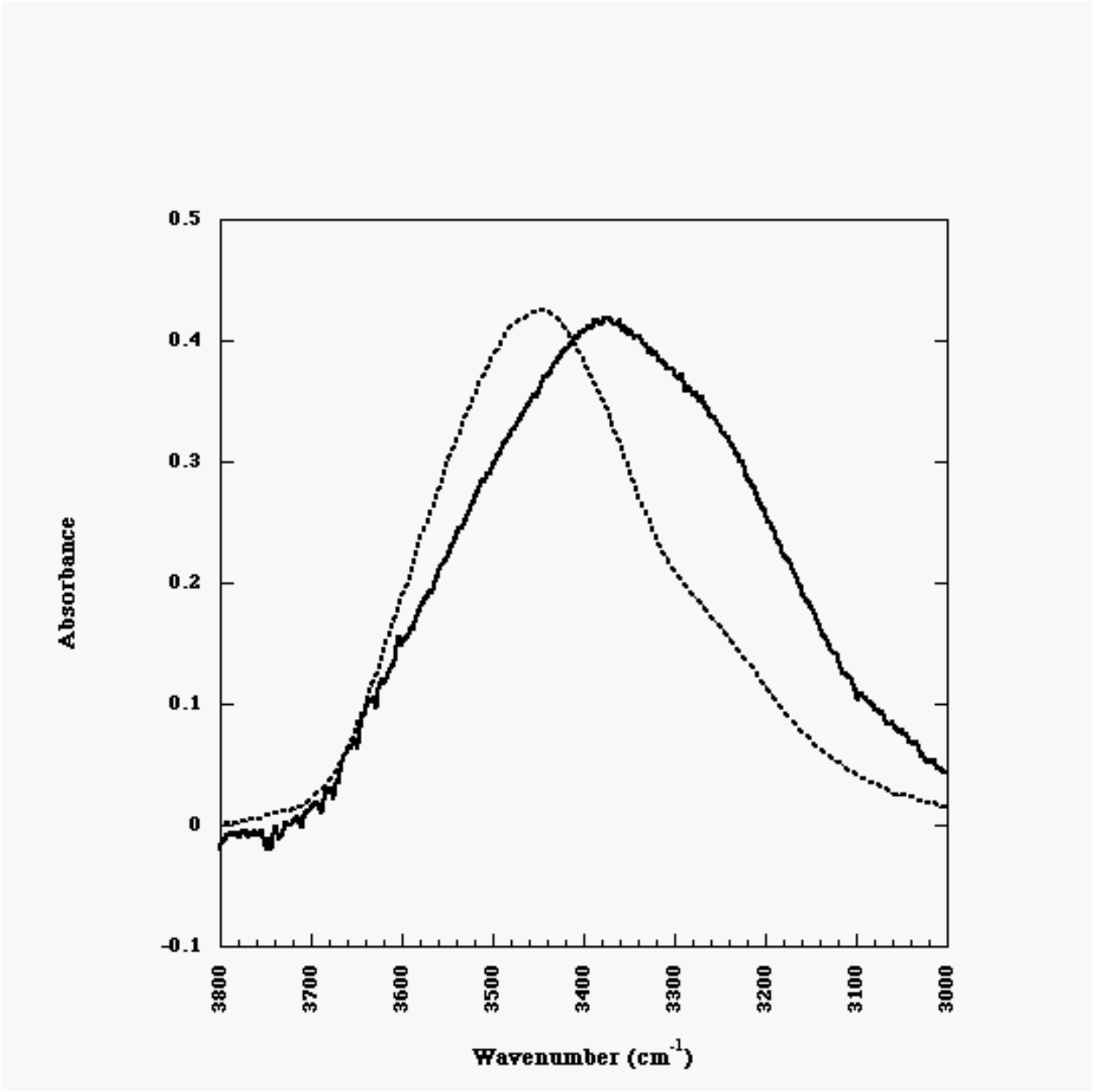
0.5
0.4
0.3
0.2
0.1
0
-0.1
Absorbance
3800
3700
3600
3500
3400
3300
3200
3100
3000
Wavenumber (cm-1)

fig1

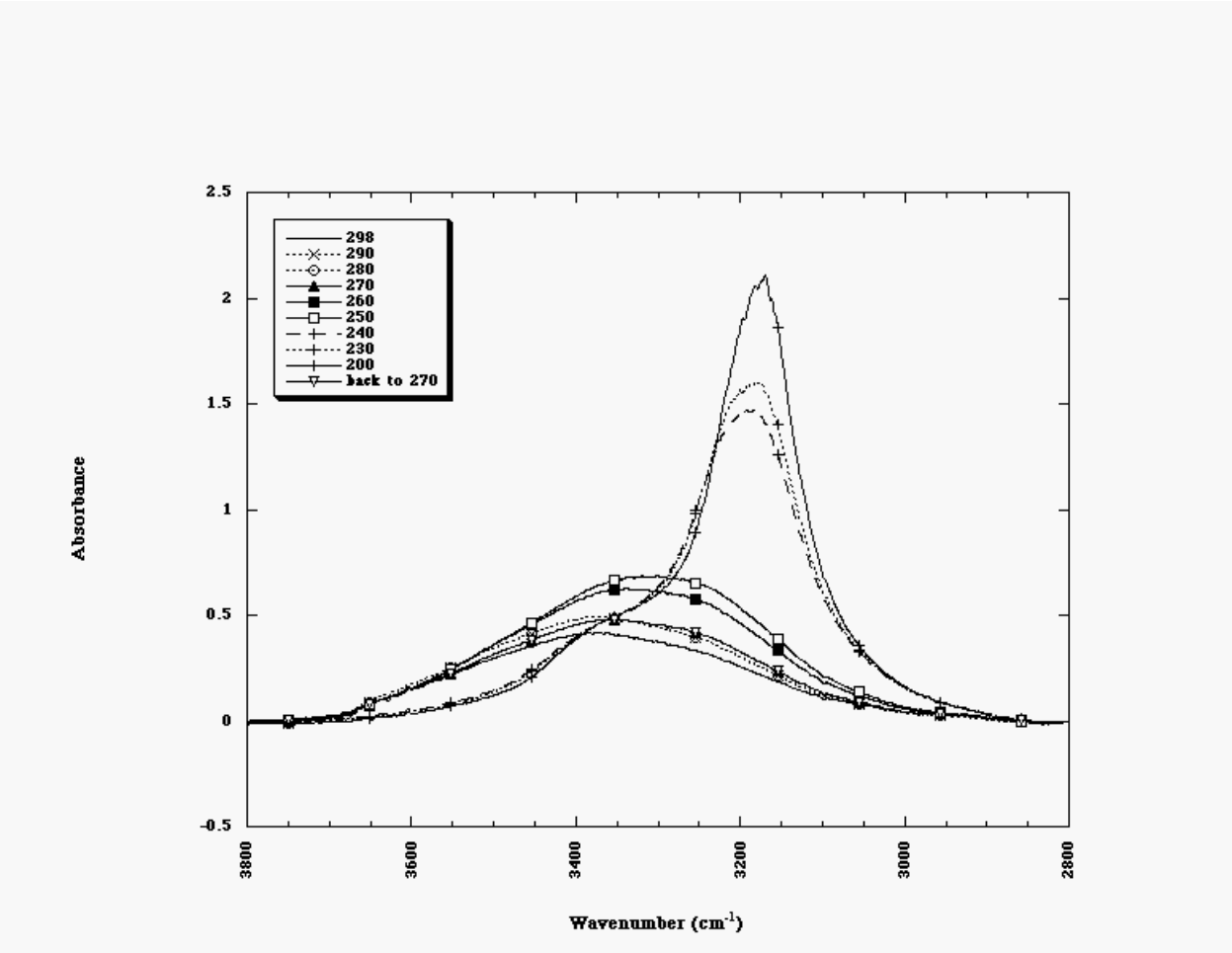
298
290
280
270
260
250
240
230
200
back to 270
Absorbance
Wavenumber (cm-1)
2.5
2
1.5
1
0.5
0
-0.5
3800
3600
3400
3200
3000
2800

fig2

Water Temperature	OH stretch peak (cm^{-1})
298K	3380
290K	3372
280K	3365
270K	3361
260K	3339
250K	3300
240K	3190
230K	3184
200K	3172
270K[a]	3360

Table I

[a] specimen cooled to 200K was warmed back to 270K

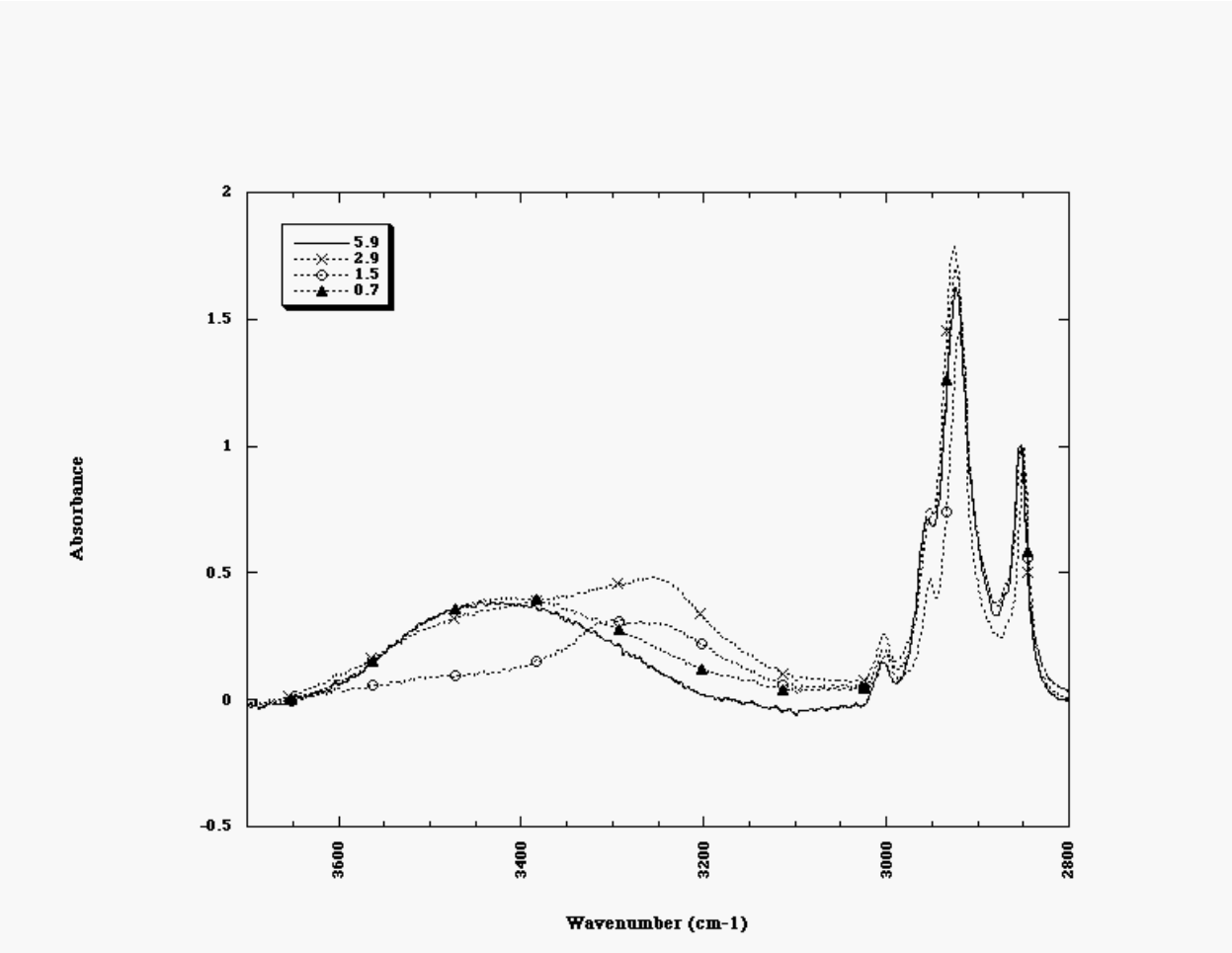
5.9
2.9
1.5
0.7
Absorbance
2
1.5
1
0.5
0
-0.5
3600
3400
3200
3000
2800
Wavenumber (cm-1)

fig3

Water: Mono-olein Molar Ratio	Appearance	OH stretch peak (cm^{-1})
5.9	clear, stiff gel	3420
2.9	cloudy, soft gel	3420, 3256
1.5	cloudy, soft gel	3295, 3262
0.7	clear liquid	3409

Table II